# FURTHER STUDIES OF PYROLYTIC PRODUCTS FROM SOME TOBACCO LEAF ACIDS

BY KIM R. GEISINGER, T. C. JONES and I. SCHMELTZ, Eastern Utilization Research and Development Division, ARS, U.S. Department of Agriculture, Philadelphia, Pa., U.S.A.

Malic and lactic acids, reportedly present in tobacco leaf, were each pyrolyzed at relatively high temperatures in an effort to compare the products thus produced with some of those present in tobacco smoke. The pyrolytic products identified included aromatic hydrocarbons, acids and phenols. A correlation was indicated between complexity of condensed ring systems (hydrocarbons) formed and pyrolytic temperature. The aromatic hydrocarbons produced during pyrolysis were typical for such reactions.

Considering the fact that tobacco leaf contains a substantial percentage of organic acids (2), we became interested in the products generated by these acids on thermal degradation (2a, 4). We were seeking to account, in part, for the composition of cigarette smoke (9). It has been previously reported (4) that a number of leaf acids, on pyrolysis, give rise to varying amounts of simple phenols found in the smoke. In related studies, Newell and Best (3a) have explored the fate of [14]C— labeled oxalic, malic and citric acids in cigarette smoke. To enlarge upon these findings, we have not examined the acidic and neutral pyrolytic products from malic acid and the sodium salt of lactic acid, both reportedly present in leaf (9). Our results are described below.

## EXPERIMENTAL

Sodium lactate and L-malic acid were each pyrolyzed under a constant flow of nitrogen in a horizontal quartz tube (2.5 cm diam. x 35 cm length) packed with quartz chips. A Lindberg Hevi-Duty Furnace[1] maintained pyrolysis temperatures: 620° ± 10°C for sodium lactate, and a series of temperatures, 500° to 900°C ± 10°C, for malic acid.

Collection of condensable pyrolytic products was facilitated by the use of three traps, the first cooled by an ice-water mixture and the latter two by Dry Ice-acetone. The product stream, after exiting the last of these traps, passed through a bubbler containing 5% sodium hydroxide solution and/or diethyl ether.

For purposes of fractionation, the pyrolysate was partitioned between ether and 5% sodium hydroxide to separate acids from neutrals (using the contents of the bubbler). The acids were further divided into phenols and carboxylic acids by appropriate pH adjustments (6). Ultimately, three fractions, each in ether, consisting of acids, phenols and neutrals, respectively, were obtained. These were dried with anhydrous sodium sulfate and concentrated, in vacuo, to a volume of 1 ml for chromatographic and other analyses.

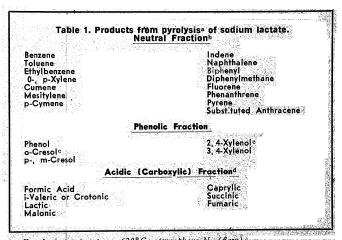A number of different techniques were used to tentatively identify the major components of ach pyrolysate

fraction. A Varian-Aerograph Model 200 gas chromatograph, equipped with dual stainless steel columns (0.25 in. O.D. x 10 ft. length) packed with 15% SE-52 on 60/80 mesh chromosorb, was used to examine the neutral and phenolic fractions. For the former, the column oven temperature was programmed from 70° to 250°C at a rate of 8°C/min. The helium flow rate was 75 ml/min, and the injector and detector temperatures were 240 and 275°C respectively. For the phenols, column temperature was maintained at 145°C; otherwise, conditions were the same as above. In some cases, acids were converted to their trimethylsilyl esters prior to gas chromatographic analysis in both programmed and isothermal modes (3).

A number of acids (5,9) and phenols (4,5) in the pyrolysates were also detected by utilizing previously described thin layer chromatographic techniques; data thus obtaind confirmed some of the GLC findings. In addition, thin layer chromatographic methods were used to look for and characterize possible carbonyl-containing compounds in the pyrolysates (1,8). Although a number of such compounds appeared to be present, we were unable to identify them.

## RESULTS AND DISCUSSION

Sodium lactate pyrolysis. On pyrolysis, sodium lactate yielded a series of aromatic hydrocarbons (Table 1), ranging from benzene to anthracene, similar to those products usually expected from relatively high-temperature pyrolysis of organic compounds (6). The neutral

### Table 1. Products from pyrolysis[a] of sodium lactate.

#### Neutral Fraction[b]

| | |
|---|---|
| Benzene | Indene |
| Toluene | Naphthalene |
| Ethylbenzene | Biphenyl |
| o-, p-Xylene | Diphenylmethane |
| Cumene | Fluorene |
| Mesitylene | Phenanthrene |
| p-Cymene | Pyrene |
| | Substituted Anthracene |

#### Phenolic Fraction

| | |
|---|---|
| Phenol | 2, 4-Xylenol[c] |
| o-Cresol[c] | 3, 4-Xylenol |
| p-, m-Cresol | |

#### Acidic (Carboxylic) Fraction[d]

| | |
|---|---|
| Formic Acid | Caprylic |
| i-Valeric or Crotonic | Succinic |
| Lactic | Fumaric |
| Malonic | |

[a]Pyrolysis temperature: 620°C; atmosphere N₂ (flow).
[b]Only 25% of neutral fraction was identified, on the basis of g.c. peak areas; all g.c. peaks were of fairly similar size. Peaks were identified by retention time comparisons, and gas cochromatography with standards, and, where possible, by the ultraviolet absorption characteristics of their corresponding effluents.
[c]Major phenols in pyrolysate: in each case, 37 mg produced per 100 g sodium lactate pyrolyzed.
[d]Components of acidic fraction were gas chromatographed as their trimethylsilyl esters (3).

compounds listed in **Table 1** were all gas chromatographable under the conditions used. We did not look for benzo (a) pyrene, although we have previously found it in pyrolysates obtained from sodium acetate (5). Interestingly, all of the aromatic hydrocarbons observed in the sodium lactate pyrolysate were produced in approximately equal amounts, based on the sizes of their corresponding gas chromatographic peaks.

The phenols **(Table 1)** generated from sodium lactate were identical to those reported previously (4), and also included 2,4-xylenol which, together with o-cresol, was present in relatively large amounts. Quantities of phenols obtained from sodium lactate, in the present study, differed from those reported earlier (4). However, the differences were not significant, and may merely deflect differences in pyrolysis conditions.

Formic acid was the predominant component of the acid fraction of the sodium lactate pyrolysate. Evidence, however, was also obtained for the presence of a number of other acids **(Table 1)**.

*Malic acid pyrolysis.* Aromatic hydrocarbons **(Table 2)** were formed at every temperature, between 500° and 900°C, to which malic acid was subjected. Toluene was the major product at 500° and 600°C, while benzene predominated at 700°C. Although there were still fair amounts of benzene, toulene and the xylenes present in the 800°C pyrolysate, the major neutral components generated from malic acid at this temperature consisted of indene, naphthalene and acenaphthylene. At 900°C, major products were chrysene, naphthalene and pyrene. As expected, the greater numbers of polynuclear aromatic hydrocarbons **(Table 2)** seem to be related to the higher temperatures of pyrolysis.

Phenols **(Table 2)** were generated from malic acid at temperatures ranging from 500° to 800°C; no phenols were found in the pyrolysate obtained at 900°C. At 500°C, the major phenolic products were phenol and o-cresol. However, at 600°C, m-cresol was the predominant product. At 700° and 800°C, relatively equal quantities of the phenols indicated were produced. The optimum temperature for production of phenols (by weight) from malic acid was observed to be 700°C.

Acids **(Table 2)** produced during the pyrolysis of malic acid included fumaric and succinic acids. The tendency for the formation of these acids was seemingly greater at the lower temperatures. Although we were unable to identify them, carbonyl-containing compounds appeared to be present in malic acid pyrolysates also, as indicated by thin-layer chromatography (1, 8).

All of the compounds identified in the malic acid pyrolysates have been reported to be present in tobacco smoke (9).

*Mechanistic implications.* A plausible pyrolytic pathway from malic acid to fumaric and succinic acids, for example, might involve dehydration of the starting material, as a first step, to give rise to fumaric acid. Hydrogenation of the latter would then yield succinic acid. The observed accumulation of water at the end of the pyrolysis tube, during malic acid pyrolysis, would lend support to such a proposed pathway, although anhydride formation would have to be considered as well.

In addition, decarboxylation of the lactic and malic acids to produce $C_2$ fragments (free radicals) may be an important step in the formation of aromatic rings via condensation reactions.

## SUMMARY

Malic and lactic acids, reportedly present in tobacco leaf, were each pyrolyzed at relatively high temperatures in an effort to compare the products thus produced with some of those present in tobacco smoke. The pyrolytic products identified included aromatic hydrocarbons, acids and phenols. A correlation was indicated between complexity of condensed ring systems (hydrocarbons) formed and pyrolytic temperature. The aromatic hydrocarbons produced during pyrolysis were typical for such reactions.

## LITERATURE CITED

1. Byrne, G. A. The Separation of 2,4-Dinitrophenylhydrazones by Thin Layer Chromatography. *J. Chromatogr.* *20:* 528-540. 1965.

2. Frankenburg, W. G. Chemical Changes in the Harvested Tobacco Leaf. Part II. Chemical and Enzymic Conversions During Fermentation and Aging. *Advances in Enzymol.* *10:* 325-441. 1950.

2a. Gilbert, J. A. S. and A. J. Lindsey. The Thermal Decomposition of Some Tobacco Constituents. *Brit. J. Cancer* *11:* 398-402. 1957.

3. Jones, T. C. and I. Schmeltz. Fingerprint Gas Chromatographic Analysis of Tobacco Leaf Acids. **Tobacco Sci.** 12: 10-15. 1968.

3a. Newell, M. P. and F. W. Best. The Fate of Oxalic, Malic, and Citric Acids in the Smoke of Cigarettes. Abstracts, 22nd Tobacco Chemists Research Conf., Richmond, Va. 1968.

4. Schmeltz, I., L. C. Hickey and W. S. Schlotzhauer. Phenols from Pyrolysis of Tobacco Leaf Acids. **Tobacco Sci.** 11: 52-53. 1967.

5. Schmeltz, I. and W. S. Schlotzhauer. 3,5-Dimethylphenol and Other Products from Pyrolysis of Sodium Acetate. *Chem. Commun.* 681-682. 1969.

6. Schlotzhauer, W. S. and I. Schmeltz. Pyrogenesis of Aromatic Hydrocarbons Present in Cigarette Smoke. II. Pyrolytic Products of Some Representative Constituents of the Hexane Soluble Fraction of Tobacco. *Beitr. Tabakforsch.* *5:* 5-8. 1969.

7. Smith, G. A. L., and P. J. Sullivan. Determination of the Steam-volatile Phenols Present in Cigarette-smoke Condensate. Part II. Determination of Phenols, Cresols, Guaiacol by Thin Layer Chromatography. *Analyst* (London) *89:* 312-318. 1964.

8. Stahl, E. Thin Layer Chromatography. Academic Press Inc. New York. 1965.

9. Stedman, R. L. The Chemical Composition of Tobacco and Tobacco Smoke. *Chem. Rev. 68:* 153-207. 1968.

10. Ting, I. P. and W. M. Dugger, Jr. Separation and Detection of Organic Acids on Silica Gel. *Anal. Biochem.* *12:* 571-578. 1965.

**Table 2. Products[a] from pyrolysis[b] of malic acid observed at various temperatures.**

| | 500° | 600° | 700° | 800° | 900°C |
|---|---|---|---|---|---|
| Benzene | ‡ | ‡ | ‡ | ‡ | ‡ |
| Toluene | ‡ | ‡ | ‡ | ‡ | ‡ |
| Indene | † | † | ‡ | ‡ | ‡ |
| Biphenyl | | | ‡ | ‡ | ‡ |
| Naphthalene | | | ‡ | ‡ | ‡ |
| Ethylbenzene } | | | † | † | † |
| m-, p-Xylene } | | | † | † | † |
| Styrene } | | | + | + | + |
| o-Xylene } | | | + | + | + |
| Dimethylnaphthalene | | | | | |
| Acenaphthylene | | | | ‡ | ‡ |
| Anthracene (Phenanthrene) | | | | ‡ | ‡ |
| Fluorene | | | | † | ‡ |
| Pyrene | | | | | ‡ |
| Chrysene | | | | | + |
| Phenol | ‡ | ‡ | ‡ | | |
| m-Cresol | ‡ | ‡ | ‡ | ‡ | |
| p-Cresol | ‡ | ‡ | ‡ | | |
| o-Cresol | ‡ | ‡ | ‡ | ‡ | |
| 2,5-Xylenol | | ‡ | ‡ | ‡ | |
| Fumaric Acid | ‡ | ‡ | + | | |
| Succinic Acid | ‡ | ‡ | | | + |

[a]Neutral products were identified by gas chromatographic retention data, and where possible, by their ultraviolet absorption characteristics. Phenols were identified on the basis of gas and thin-layer chromatographic studies; the presence of m-cresol was confirmed by ultraviolet absorption studies, as well. Carboxylic acids were characterized by thin-layer chromatographic methods (10,8).
[b]Under nitrogen flow.